2001 Annual Report

RESEARCH AND REFERENCE ACTIVITIES

Laboratory Services Branch
Ontario Ministry of the Environment

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Overview

Research and reference activities remain a small but important part of the workload at the Laboratory Services Branch (LSB). During the past year the LSB focussed its efforts on support of ministry priorities relating to the new Drinking Water Protection regulation and enforcement of regulations.

This year, organic analytes dominated the overall R&D effort, as only one project is reported that involved inorganic analyte parameters. In addition, projects devoted to microbiological parameters appear for the first time since 1995. The emphasis on organics is not surprising – as chemicals are developed for industrial and agricultural applications on an ongoing basis, and it may require decades to assess the full environmental impact of even a few of them. Methods are required to monitor these compounds at low detection limits in virtually every type of environmental sample. This work is difficult, because many of the compounds are chlorinated aromatics that have to be separated from one another to avoid interferences, and because of the low detection limits required.

For further information on any of the projects or activities described in this report, readers are directed to the Study Leader, or to the Author:

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A. New Applications of Technology

Introduction

The evaluation of Time-of-Flight Mass Spectrometry (TOFMS) for environmental analysis applications (reported last year) has been greatly expanded as a result of a partnership with LECO Instruments Canada. As TOFMS was shown to be a promising technology for multi-analyte environmental determinations, four Laboratory Services Branch Sections are involved in this technology evaluation project. One of the important advantages of TOFMS is the ability to scan the output of a gas chromatography column much more rapidly than can be done using other conventional mass spectrometer technologies. This makes TOFMS an excellent candidate as the detector of choice for Fast Gas Chromatography (Fast GC) applications. Fast GC allows greater resolution of complex environmental samples, or faster analysis times compared to conventional GC applications with no loss of resolution. Therefore, the combination of Fast GC with TOFMS may result in faster, more cost-effective organics determinations.

Other development work that involved relatively new technologies included studies on using Pressurized Fluid Extraction, and Liquid Chromatography–Mass Spectrometry (LC-MS). The pressurized fluid extraction studies first reported last year have been very successful, as a number of LSB methods are being revised to include this technology as a preferred method of solid sample extraction. The use of LC-MS for microcystins shows why LC-MS methods for environmental contaminants are becoming so important – there are many analytes not suited to the more conventional gas chromatography-based methods.

I. LC-(Electrospray Ionisation) MS Determination of Microcystins and Nodularin

Study Leader:	Steve Jenkins [Mass Spectrometry Section]
Study Team:	Vince Taguchi
Customer:	Environmental Monitoring and Reporting Branch, Standards Development Branch

Objective

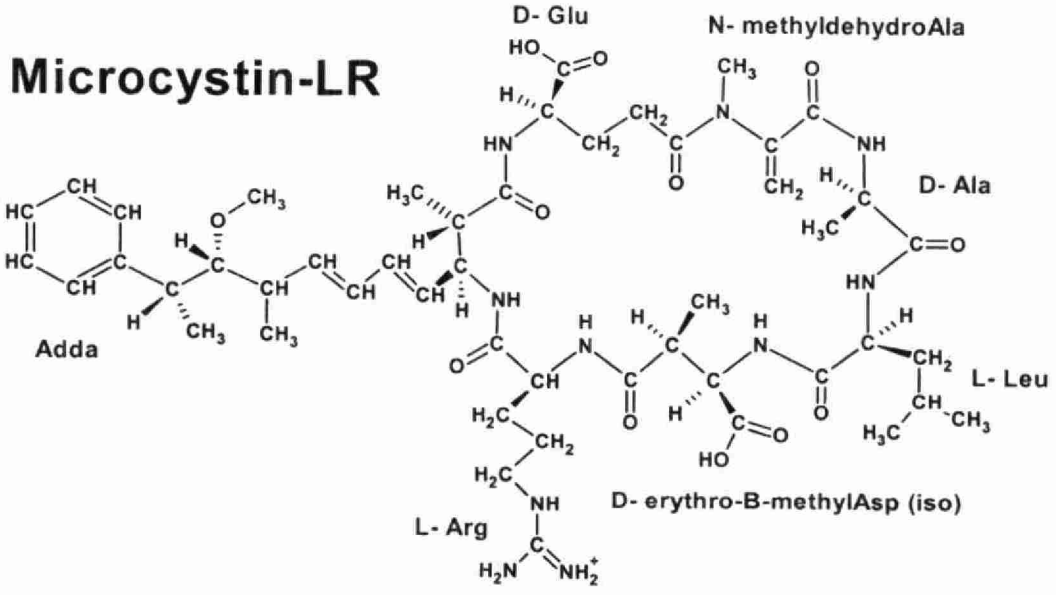
To develop a quantitative analytical method for microcystins and nodularin in drinking water and surface waters by Liquid Chromatography - (Electrospray Ionisation) Mass Spectrometry [LC-(ESI)MS].

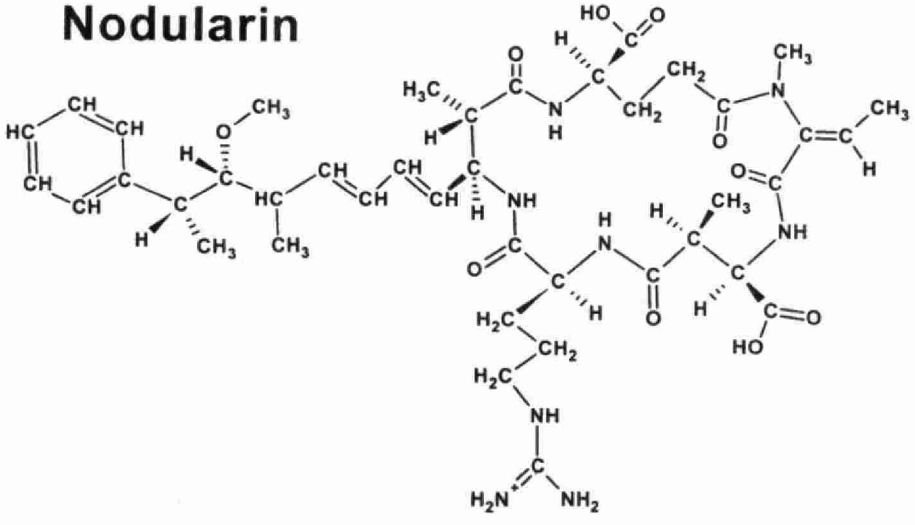
Background

Microcystins are cyclic heptapeptide hepatotoxins produced by cyanobacteria (blue-green algae; see structure below). Nodularin is a cyclic pentapeptide. Genera known to produce hepatotoxins include *Microcystis*, *Planktothrix (Oscillatoria)*, *Aphanizomenon, Anabaena* and *Nostoc*. So far, more than 50 microcystins have been identified. Microcystins have been responsible for the poisoning of fish, birds and animals in many countries. In 1996, over 40 patients undergoing dialysis treatment, in the Brazilian city of Caruaru, died from microcystin poisoning from contaminated water. Microcystins have also been found to be tumour promoters. The most toxic and most abundant congener is microcystin-LR. The intracellular toxins are released at the later stages of the cell's life cycle or when water is treated with an algicide which lyses the cell wall. The toxicity of microcystin-LR is related to its irreversible inhibition of the protein phosphatases 1, and 2A required for the proper regulation of cell metabolism.

Results

Previously, a procedure was developed for the analysis of soluble microcystin-LR in drinking water using C18 SPE disks. However, it was discovered that the toxin could be extracted from water using bulk C18 SPE material. This made the method less





costly as well as more reproducible. The microcystin-LR is quantified by using the internal standard Gramicidin S (a cyclic decapeptide antibiotic). The detection limit with the bulk C18 SPE material remained the same as before, approximately one order of magnitude below the proposed drinking water guideline of 1.5 µg/L. The microcystins and nodularin are analysed by electrospray using a tandem triple quadrupole mass spectrometer. The instrument is used in the single quadrupole selected ion recording mode, but is capable of MS-MS analysis (increasing specificity) should the need arise to reduce the effect of interferences.

Current Status

The original scope of the project was for the analysis of microcystin-LR only in drinking water. This has since expanded to include the microcystins -RR, -YR, -LA and nodularin. The microcystins -LF, and -LW have also been incorporated into the method, but due to their inconsistent commercial availability, may or may not be included.

II. Evaluation of GC-Time-of-Flight MS for the Determination of Toxic Organics

Study Leader:	Adrienne Boden [Dioxin & Toxic Organics Section]
Study Team:	Eric Reiner
Customer:	LECO Instruments, all customers of DTO Section

Objective

To evaluate the use of gas chromatography time-of-flight mass spectrometry (GC-TOF) for the analysis of toxic organic compounds in environmental samples.

Background

In order to improve analysis speed, *Fast GC* has been investigated in recent years. Two of the key factors in *Fast GC* are shorter columns and faster oven temperature programming rates. Both result in some loss in chromatographic resolution, however, this loss may be offset by the use of thinner stationary phase films and smaller column internal diameters. The majority of analytical methods in DTO have now been converted to *Fast GC* methods using microbore columns. Analysis times have been reduced by up to a factor of 5. As *Fast GC* techniques advance producing faster sample separations and extremely narrow analyte peak widths, faster detection methods have become necessary. Conventional mass spectrometric detection methods such as quadrupole mass spectrometry (MS) or high resolution mass

spectrometry (HRMS) are limited by relatively slow MS scan speeds. This hinders the accurate identification and quantification of *Fast GC* peaks, thereby lengthening the time required for sample analysis. Time-of-flight (TOF) mass spectrometers have the advantage of much faster scanning rates compared to conventional MS methods. It is expected that the benefits of *Fast GC* can be extended much further by the use of TOF-MS detection.

Results

Three companies that manufacture TOF-MS instruments – Leco Corporation, Micromass UK Ltd. and Thermo Finnigan – were sent test samples for analysis. Initial results were encouraging for many of the analytes selected. Problems encountered included variable sensitivity for some compound classes, especially higher boiling analytes and GC peak tailing for planar molecules like PAH with molecular weights greater than or equal to 250 Da. Initial data from the manufacturers indicate that most PCBs, OC Pesticides and PAH may be selectively determined using *Fast GC* analysis. Deconvolution of analyte peaks has been impressive using the Leco instrument. Micromass uses an alternate approach - a higher instrument resolution of 5000 compared to the unit resolution achievable by the Leco mass spectrometer. None of the instruments could meet the 1 pg detection limit required for all analytes tested.

Research has been performed by this study team on a GC-TOF instrument located at MOE-LSB. The GC-TOF was evaluated using different chromatographic columns (10 m DB-5, 0.18 mm id, 0.18 µm film thickness; 20 m DB-5, 0.1 mm id, 0.1 µm film thickness) for the analysis of toxic organic compounds. Development of a "mega method" for the single-run quantification of polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides and polycyclic aromatic hydrocarbons (PAH) is currently being evaluated. We have developed a method that has the advantage of detecting and quantifying 117 different analytes spanning three compound classes in one rapid analysis (see Table 1). A determination of this scale is normally performed using three different analytical runs on different instruments; each analytical run taking from 23 - 45 minutes. This new application using a DB-5 chromatographic column (10m, 0.18 mm id, 0.18 µm film thickness) achieves the detection and quantification of 117 analytes in a single 7 minute analytical run.

Table 1: Scope of the analytes determined and analysis times achieved using *Fast GC*-TOF.

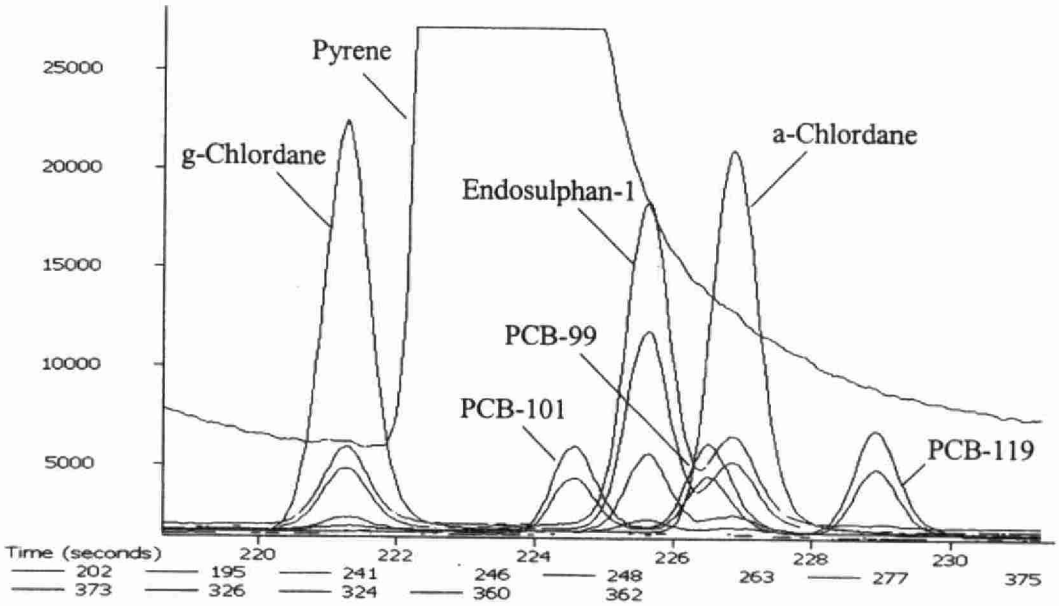
Compound Class	Number of Analytes in Standard Mixture	Elution time achieved for all analytes of each compound class (min.)	Calibration Curve Correlation Coeff.: R (5 concentration levels, n=3 for each level)
PAH	36 (inc. internal stds.)	6.7 minutes	0.992 - 0.999 (128-292 Da range)
PCBs	61	5.8 minutes	0.999 (di-substituted) 0.992 (deca-substituted)
OC Pesticides	20	5.0 minutes	0.998 - 0.999
Totals	117	Total Analysis Time: 7.3 minutes	

Five-point calibration curves (using triplicate analyses) constructed for each compound class yielded correlation coefficients for linearity (R) exceeding 0.99 (see Table 1). Detection Limits for each compound class for a GC-TOF injection of one microliter varied from about 5 - 100 picograms injected. Detection limits can be lowered using larger injection volumes. Coelution of certain PCBs was observed; most could be deconvoluted by the GC-TOF software. Using GC with electron-capture detection, separation of PCB critical pairs, such as IUPAC# 81/87, 77/110, 123/149, 157/201 are difficult; samples must be analysed twice using different stationary phases in order to separate and accurately quantify the individual congeners. Using the GC-TOF method, these critical pairs were deconvoluted (on the basis of mass spectral differences) enabling their quantification in a single 7.3 minute analysis. Quantification of the total sum of two co-eluting PCBs was required in only a few cases where the analytes were of the same congener group and were unresolved both chromatographically and spectrally (same molecular mass and near-identical mass spectra).

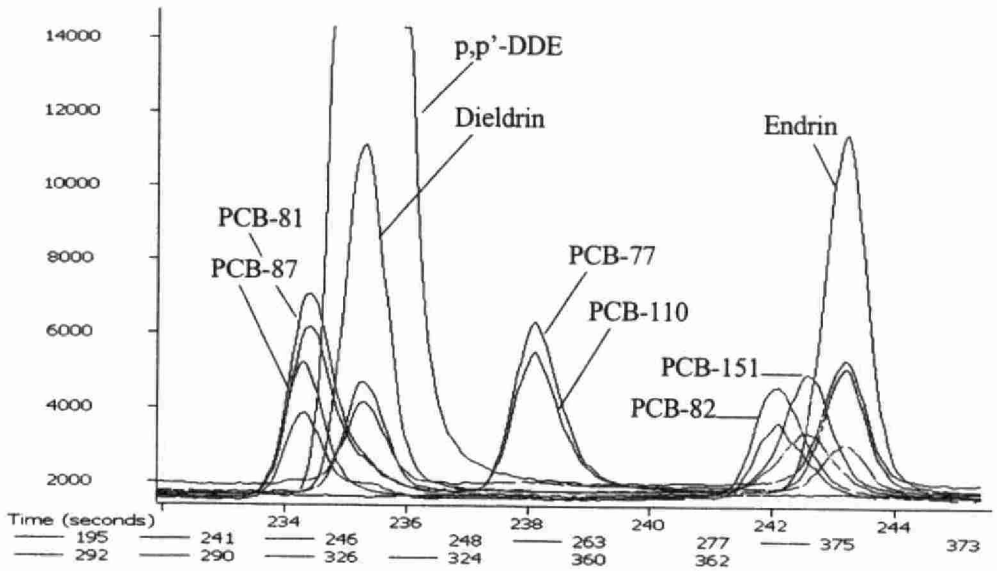
Overall TOF instrumental sensitivity was worse for high molecular weight compounds, and peak-tailing was a problem for large planar aromatic compounds like PAH. Increasing the ion source temperature from 250°C (standard running temp.) to 300°C provides an 1.5 to 2-fold increase in sensitivity for high mass PAH. The increase in source temperature also resulted in a reduction in chromatographic peak tailing and an increase in chromatographic resolution for critical compound pairs.

Figure 1: GC-TOF chromatograms showing the simultaneous separation and determination of PAH, PCBs and organochlorine pesticides (total analysis time: 7.33 min on a 10 m DB-5 column).

A)



B)



The GC-TOF chromatograms in Figure 1 show the simultaneous separation and deconvolution of a mixture of PAH, PCB and organochlorine pesticides. Analyte concentrations in this solution varied over a 40-fold range. Under these *Fast GC* conditions the chromatographic peaks elute very closely. In chromatogram (A), a total ion chromatogram would suggest the presence of 3 analytes. It can be seen that there are actually 7 analytes, the majority of which would be masked by the Pyrene peak if conventional detection methods were used. In chromatogram (B) of Figure 1, although many of the analytes partially or completely coelute, all of the analytes are spectrally deconvoluted and can thereby be quantified individually. Critical coeluting pairs such as PCB-81/PCB-87 and PCB-77/PCB-110, that are normally difficult to quantify using conventional methods, are easily managed in this rapid analysis.

Current Status

This "mega method" appears to have potential as a robust screening method for PAH, PCBs and OC pesticides and must be further evaluated with samples from various environmental sample types. If instrumental sensitivity is improved, preliminary results indicate that GC-TOF may be able to achieve the required data quality objectives (DQOs) for the analysis of environmental samples. Manufacturers have been requested to change their instrument designs to allow for additional hardware parameter changes and for operation of the transfer-line and ion source at higher temperatures; we feel these changes will reduce GC peak tailing and improve detection limits for many analytes. Analytical conditions targeted to increase sensitivity for the determination of dioxins, furans and dioxin-like compounds should be investigated. We would also like to explore the use of GC-TOF for new *Fast GC* methods and multi-dimensional methods using microbore columns with different stationary phases.

III. GC/TOF-MS Analysis of Toxicity Characteristic Leaching Procedure (TCLP) Samples

Study Leader:	Chunyan Hao [Applied Chromatography]; LECO Instruments
Study Team:	Paul Yang
Customer:	George Kanert [Physical Chemistry & Litigation Section]

Objective

To evaluate the use of a gas chromatography/time-of-flight mass spectrometer (GC/TOF-MS) system for the analysis of Toxicity Characteristic Leaching Procedure (TCLP) samples described in Ontario Regulation 347.

Background

Several leaching procedures can be used to simulate natural environmental leaching process for the evaluation of toxic characteristics of a waste. The Toxicity Characteristic Leaching Procedure (TCLP) described in Ontario Regulation 347, a test described under the U.S. Federal Resource Conservation Recovery Act (RCRA), is commonly used for this specific purpose. Ontario Regulation 347 requires the quantitation of 88 toxic environmental pollutants to characterize the toxicity of a TCLP sample. Thirty-nine of these analytes are semi-volatile organic compounds (SVOCs) that are not thermally labile and can be analyzed using a GC based analytical method. We report here a fast GC/TOF-MS based "mega-method" for the effective, high throughput analysis of 39 TCLP SVOCs target compounds encompassing five compound groups specified in Ontario Regulation 347.

Results

Custom prepared TCLP standards were purchased from Chromatography Specialities (Brockville, ON). The GC/TOF-MS system consisted of an Agilent 6890 GC (Little Falls, DE) and a LECO Pegasus III TOF-MS (St. Joseph, MI) system. The GC was equipped with a split/splitless injector, an electronic pressure controller (EPC), and a 20m x 0.15mm x 0.15mm Valco VB-5 GC column (Gig Harbor, WA). Helium was

used as the carrier gas and the EPC was operated in the constant flow mode using a flow rate of 1.8 mL/min. The typical sample injection volume was 3 mL, GC injector, transfer line, and ion source temperatures were set at 220˚C, 250˚C and 250˚C, respectively. All mass spectra were acquired in electron impact ionization mode, pulsed at 5,000 kHz, collected at a data acquisition rate of 15 spectra/sec, and processed with ChromoTOF software provided by LECO. The ChromoTOF software consists of the automated peak-finder and chromatogram deconvolution software which allowed positive identification of GC eluents via full mass spectral library search and quantitation.

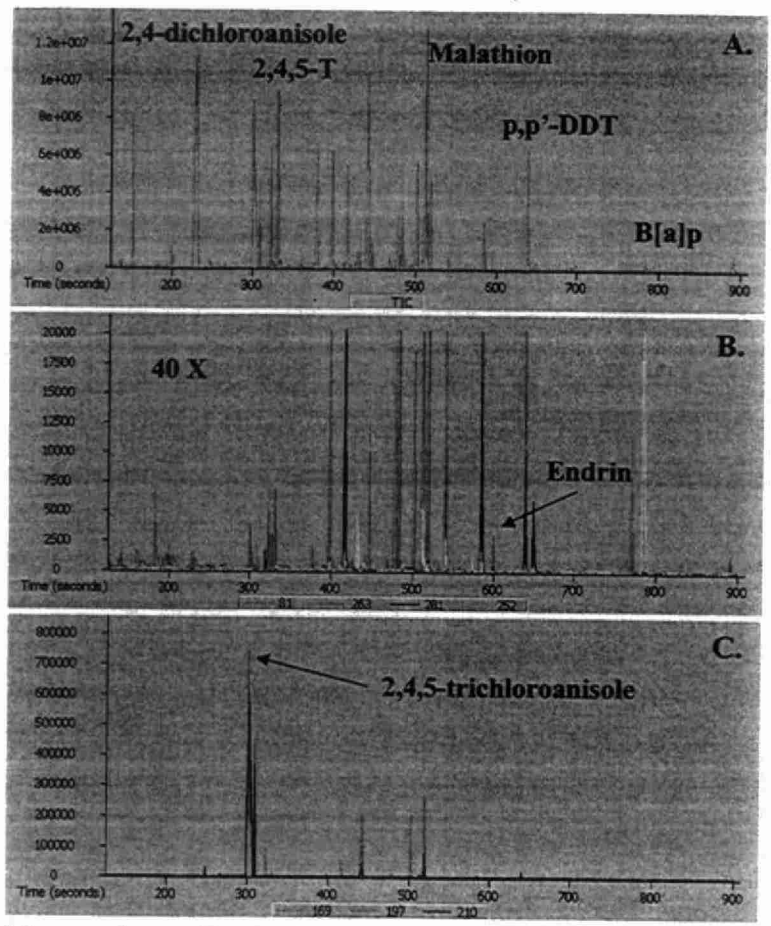


Figure 1. Typical reconstructed GC/TOF-MS ion chromatograms of TCLP analysis.

One can separate the 39 Regulation 347 SVOCs into five distinct groups of pesticides and herbicides. These include 12 chlorophenol and phenoxyacide (CP/PA) herbicides, 11 organochloride (OC) pesticides, 10 organophosphorus (OP) pesticides, 5

nitrogen-containing herbicides (triazines), benzo[a]pyrene. Current analytical parameters allowed the separation and identification of these 39 SVOCs by a 16 minute GC/TOF-MS analysis. The typical GC/TOF-MS reconstructed chromatogram is shown in Figure 1A. There are four groups of coeluting GC peaks. The Manufacturer-supplied software uses a peak-finder, which performs a full spectral library search for peaks with a predefined signal-to-noise ratio and determines unique mass(es) of each compound, and mathematically de-convolutes and derives the mass spectra of the overlapping compounds. This procedure minimizes the interference from the co-eluting target compounds and contaminants, provide better EI mass spectra for better library search, and quantitative analysis results. The resolution loss resulting from fast GC separation was thus well compensated by the fast data acquisition of the TOF-MS and deconvolution. Thus, the identification and quantification of analyte in a complex mixture can be achieved with confidence with the reduction of long and tedious data interpretation time. Upon establishing the absolute sensitivity, TCLP standards were tested at four concentration levels (1, 1/2, 1/5 and 1/10 of target's TCLP regulation concentration). At concentrations of approximately 1 and ½ of the Regulation level, calculated concentration of each target matched very well with the expected values (within 10% of standard deviation, STD). At lower concentration levels, i.e., approximately 1/5 and 1/10 of the regulation concentration for targets, more than 10% of the STD were observed for several compounds. Current method does not work for 2,4,5-Trichlorophenol when its concentration goes below 1/5 of the regulation level as it falls out of the linear range. Efforts are being made to find a way for the analysis of 2,4,5-Trichlorophenol at this concentration level.

The TOF-MS system exhibited a high dynamic range which can be crucial for TCLP analysis. For example, endrin and 2,4,5-trichlorophenol (2,4,5-TCP) are regulated at concentrations of 400 and 0.02 mg/L in Regulation 347. These correspond to a column loading of 1,200,000 and 60 pg, for 2,4,5-TCP and endrin, respectively, (3 μL injection volume). The reconstructed total ion chromatogram (Fig. 1A) was dominated by 2,4-dichlorophenol (2,4-DCP, analyzed as 2,4-dichloroanisole) and one could not see the endrin peak even at 3X regulatory levels (180 pg column loading). In Figures 1B and 1C, both compounds are detected in a single analysis. Therefore, the use of large sample volumes, low dilution factors, high injection volumes (up to 5 μL), and multiple characteristic ions, were used to increase the sensitivity (e.g., endrin) and maintain system linearity (e.g., 2,4,5-TCP) so that target compounds having greatly differing concentrations can be handled with a single method. Table 1 shows the performance of the GC/TOF-MS system for standards at various concentrations.

Table 1. Performance of TOF-MS for TCLP Standards at Various Concentration Levels (OCs and B[a]p are at 3 and 500 times of Regulation levels while chlorophenols and phenoxyacids, organophosphorus, and nitrogen-containing pesticides are at approximately Regulation levels, N = 9.

Name	Expected	Average Total ng	Std. Dev.	RSD
Ethane, hexachloro-	9000	8495.7	577.6	6.8%
Hexachlorobutadiene	1500	1493.0	43.7	2.9%
2,4-Dichloroanisole	90000	87517.7	3325.8	3.8%
2,4,6-Trichlorophenol	500	500.5	14.0	2.8%
2,4,5-Trichlorophenol	400000	408438.1	11308.5	2.8%
Dicamba methyl ester	12000	12290.4	156.0	1.3%
Bromoxinil	500	503.7	18.7	3.7%
2,4-D methyl ester	10000	10773.2	199.5	1.9%
Trifluralin	13500	14398.8	221.7	1.5%
Phorate	200	191.8	7.4	3.8%
Hexachlorobenzene	390	393.7	8.4	2.1%
Pentachloroanisole	6000	6110.9	108.3	1.8%
Dimethoate	2000	2149.0	40.6	1.9%
Simazine	1000	996.1	26.0	2.6%
Atrazine	500	494.0	13.0	2.6%
Silvex (2,4,5-TP)	1000	1024.0	28.3	2.8%
BHC	1200	1209.4	29.0	2.4%
Terbufos	100	96.4	3.2	3.3%
2,4,5-T Methyl ester	28000	28711.4	445.7	1.6%
Diazinon	2000	1966.8	39.4	2.0%
Dinoseb, methyl ester	1000	952.7	37.2	3.9%
Metribuzin	8000	8579.5	143.2	1.7%
Methyl parathion	5000	5357.9	107.5	2.0%
Heptachlor	900	883.4	19.1	2.2%
Pichloram methyl ester	20000	21678.9	254.1	1.2%
Aldrin-R	3000	3061.5	47.3	1.5%
Malathion	20000	20539.3	243.8	1.2%
Metolachlor	5000	5402.7	71.6	1.3%
Dursban	5000	5256.4	73.2	1.4%
Cyanazine	1000	1050.8	22.7	2.2%
Parathion	2000	2025.0	52.3	2.6%
Heptachlor epoxide	900	913.4	17.7	1.9%
Dieldrin	3000	2927.5	70.8	2.4%
Endrin	60	59.0	3.5	5.9%
p,p'-DDT	9000	9614.7	111.7	1.2%
Dichlorofop methyl	1000	978.1	39.8	4.1%
Azinphos-Methyl	2000	2000.9	59.1	3.0%
Benzo[a]pyrene	500	484.0	17.8	3.7%
Temephos	28000	26818.8	877.9	3.3%

Current Status

The method development is complete. A new method based on this work is being documented in preparation for audit.

IV. Dual-Column Fast GC Determination of Toxic Organics

Study Leader:	Karen MacPherson [Dioxin & Toxic Organics Section]
Study Team:	Terry Kolic, Eric Reiner
Customer:	Environmental Monitoring & Reporting Branch, Drinking Water and Fish Contaminants Programmes

Objective

To significantly reduce analysis times for Dioxins/Furans/Co-planar PCBs and mono-ortho PCBs by simultaneous injection of different clean-up fractions on microbore GC columns.

Background

Analyses for Dioxins/Furans and DLPCBs are commonly carried out in two separate analytical runs on a GC/HRMS instrument. Collectively the analyses require about 80 minutes and are typically run over a period of two days to incorporate required QC analytical runs. The use of microbore Gas Chromatography (GC) columns to reduce analysis times by 50-80% with Fast GC (column head pressures of >60psi and temperature ramp rates of >75°C/min.), has been demonstrated previously for a variety of organic analytes [1]. With Fast GC techniques optimum GC column configuration was established for Dioxin/Furans and Coplanar PCBs on a 40m x 18mm x 180µm, 5% phenyl microbore column. Simultaneous analysis of mono-ortho substituted PCBs was carried out on a 20m x 10mm x 100µm, 5% phenyl microbore column.

Results

A sample clean-up scheme (MOEE Method 3418) was originally developed to force Polychlorinated Diphenyl Ethers (PCDEs) into the mono-ortho DLPCB fraction, to ensure complete separation from the PCDD/Fs clean-up fraction. Subsequently, for simultaneous injection of these two fractions on dual GC columns, GC conditions were developed to elute the mono-ortho DLPCBs from a 20m GC column before the elution of PCDFs and PCDDs from a 40m GC column. With simultaneous injection on parallel columns, all of the congeners in the mono-ortho DLPCB fraction (with the exception of PCB 189) elute from the 20M column before the PCDDs/Fs elute from the 40M column.

GC parameters were optimized to maintain critical congener separations required for PCDD/F analysis and PCB123 and PCB 118 for DLPCB analysis. Experimentally it has been determined that 175,000 plates are required to obtain the necessary separation of 2,3,7,8-TCDD from 1237/1238-TCDD. This criterion can be met on the 40M Rtx5 column which is reported to contain 212,000 theoretical plates by Restek[2]. Additionally, group totals can also be determined on the 40m microbore columns which actually have more theoretical plates than the conventional 60m column. Data from various sample types and from a number of certified reference materials, generated by using this dual-GC column method, show excellent agreement with the data generated by conventional GC/HRMS analyses [3].

Current Status

Method Detection Limits (MDLs) are required to validate the method for application to the analysis of various sample types.

Publications

[1] K.A. MacPherson, E.J. Reiner, R.Brunato, T.Chen, M.A. Bogard, A.R.Boden and G.Ladwig. Analysis of Persistent Organic Pollutants (POPs) using microbore columns, Organohalogen Compounds,(2000), 45, 17-20.

[2] K.A. MacPherson, E.J. Reiner and T.M. Kolic. Dual Microbore Column GC/HRMS Analysis of Polychlorinated Dibenzo-p-dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs) and Dioxin-Like Polychlorinated Biphenyls (DLPCBs). Organohalogen Compounds (2001), 50, 40-44.

B. Methods Development

Introduction

The majority of method development projects reported here were initiated in 2001, about 60% of the total projects. This shows a continuation of a recent trend towards more focussed development work, where fewer projects are active, but completion times are generally shorter. To maximize the effectiveness of limited resources available for R&D projects, LSB customers have become part of the project planning process – in part by establishing the absolute priority of their method development requests.

The projects this year involved a wide range of environmental sample types. Methods for various organic analytes in air, drinking water, toxic leachate, and biosolids were developed. The development of new microbiology methods is reported for the first time in five years. Many of the methods studied were for groups of compounds that contained many different isomers and/or congeners, including the polycyclic aromatic hydrocabons (PAH), brominated diphenyl ethers, polychlorinated naphthalenes, and toxaphene.

I. Method for Acetonitrile in Air

Study Leader:	Mike Sage [Mass Spectrometry Section]
Customer:	Standards Development Branch

Objective

To develop an adsorbent cartridge/thermal desorption and GC/MS method for the trace level testing of acetonitrile in ambient air in support of the Standards and Development Branch Standards Setting Plan. Currently, an air standard does not exist in Ontario for acetonitrile, therefore data quality objectives (DQOs) have not been finalized.

Background

The Ministry of the Environment maintains a listing of more than 300 ambient air quality criteria (AAQC) and their corresponding point of impingement (POI) limits. AAQCs are used for assessing general air quality, and the potential for specific pollutants causing adverse effects. POI limits are used primarily to review applications for Certificates of Approval for emissions to air and to assess compliance with Ontario Regulation 346. The ministry has placed specific emphasis on reviewing and updating existing air quality standards to ensure that they are current and protective of human and ecosystem health.

The 1996 plan identified 101 substances as candidates for air standards development. Since that time the ministry has undertaken a comprehensive new review of the air standards and has placed air standards into one of two groups. Group 1 contains substances that are considered as high priority candidates for air standard development based on toxicity, releases to the atmosphere in Ontario, and identification as priorities by federal and national committees. Acetonitrile is in the subset of 70 compounds from Group 1 that are high priority air standards to be reviewed by the ministry.

Results

A viable method for the analysis of acetonitrile in air samples collected on Carbotrap 300 (contains 3 adsorbents - Carbotrap C, Carbotrap B, Carbosieve S-III) adsorbent cartridges for preconcentration followed by gas chromatography on a 60 metre Restek RTX-502.2 1.8 µm column and mass spectrometry has been developed. The active layer for acetonitrile is Carbosieve S-III. The method is suitable for the analysis of acetonitrile in ambient air. The limit of measurement (W), limit of reliability (T) and method detection limit (MDL) were determined by following protocols described in the Laboratory Services Procedure Manual (LSBSOP.026). Acetonitrile values for W, T and MDL were 0.01, 0.1 and 0.02 µg/m^3 respectively based on a typical network sample volume of 7.2L (for a 3L volume results are 0.02, 0.2 and 0.1).

Instrument within-run precision for acetonitrile based on an analysis of a set of 8 standards at 0.2 ug/m^3, and for a set of 11 standards at 8 µg/m^3, was <7% relative standard deviation. Average concentration of acetonitrile in sample blanks was 0.028 (7.2L) and 0.067 (3L) µg/m^3. Acetonitrile recovery is dependent on the amount of water collected in the sample. Water is removed from the sample by passing a dry gas (helium or nitrogen), at approximately 30 mL/minute, through the cartridge (heated to 40°C). The amount of dry purging required (in minutes) must be increased as water content increases, which may result in lower acetonitrile recoveries. A set of duplicate field spikes yielded recoveries of 40 - 95 % depending on the amount of water retained by the cartridge. Measured quantities of water in this set ranged from 1 to 9 mg. To compensate for variable recovery a spiked field sample should be run upwind of the sample location when field samples are collected.

A correlation coefficient of 0.996 was achieved for acetonitrile over a range of 1.0 to 224 total ng loading. By employing flexible sampling periods and sample flow rates the method can be applied for both AAQC and point of impingement monitoring applications.

Current Status

Method VOCAIR-E3314 must be modified to include performance data for acetonitrile. Product VOC3314 in LIMS requires modification. The method is essentially complete, subject to audit.

II. Method for PAH in Soil & Sediment by Isotope Dilution GC-MS

Study Leader:	Adrienne Boden [Dioxin and Toxic Organics Section]
Study Team:	John Bodnar, Eric Reiner
Customer:	Standards Development Branch (Phytotoxicology), Region Operations Division and Environmental Monitoring and Reporting Branch (Surface Water Surveillance)

Objective

To develop an isotope-dilution gas chromatography mass spectrometric (ID GC-MS) method for the determination of polycyclic aromatic hydrocarbons (PAH) in soil, sediment and biota. This new method uses isotopically-labelled analogues of the PAH of interest to compensate for variable recovery of PAH during sample preparation and for the effects of instrumental variables, and therefore improves the precision and accuracy of quantitative data.

Background

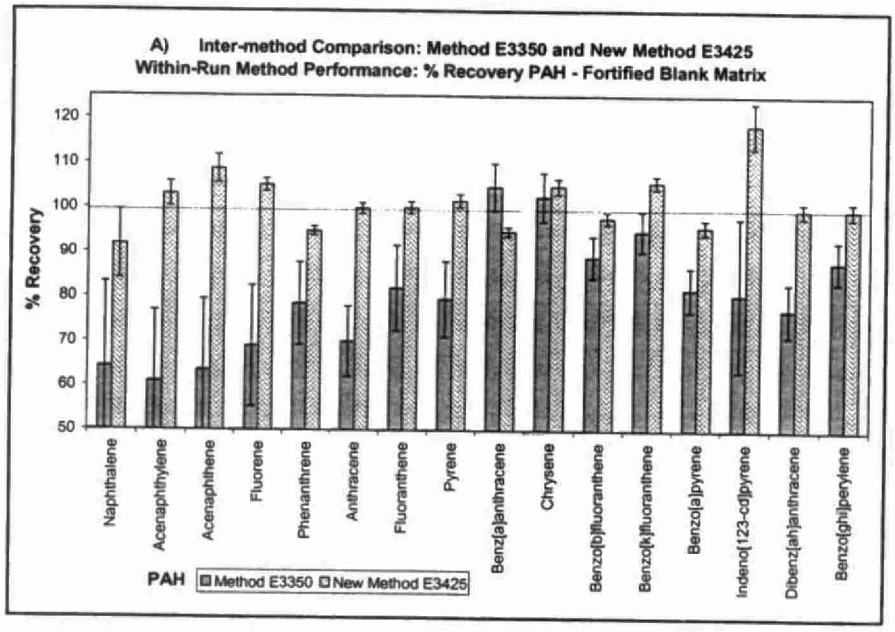
Polycyclic aromatic hydrocarbons are one of the largest single classes of chemical carcinogens known today. PAH are formed during the incomplete combustion of carbon-based fuels and have been found to be ubiquitous environmental pollutants. In order to improve data quality for the determination of PAH in environmental samples, lower limits of detection are required while maintaining acceptable precision and accuracy. Unfortunately, the accuracy of quantitative data often suffers due to sample losses during extraction, clean-up procedures and general sample handling in the laboratory. Such losses can be determined and compensated for by spiking samples with stable isotope analogues of analytes. It is assumed that the losses of the stable isotopically enriched compounds occurs at the same rate as the native analytes. Because mass spectrometers can distinguish native analytes from their isotopically enriched analogues, this "isotope-dilution" technique can be used to correct for sample losses through sample preparation.

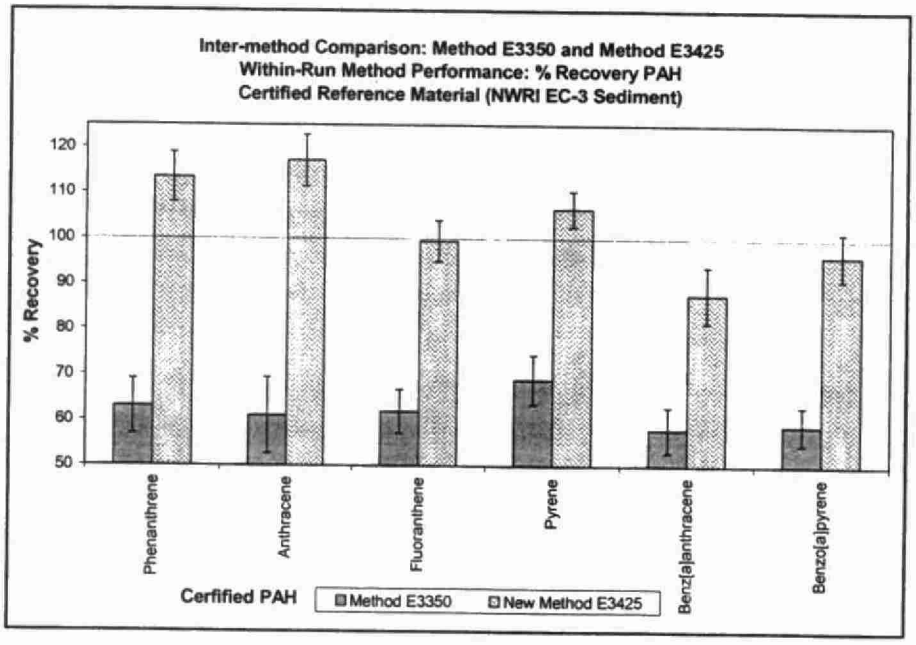
Results

This new method is designed to replace the current LSB method E3350. Method E3350 utilizes: (i) a lengthy sonication/robotic extraction procedure requiring large amounts of solvent, (ii) manual nitrogen evaporating steps, (iii) a single-point calibration, and (iv) does not account for analyte recovery in the quantification of all PAH. This new method utilizes: (i) a rapid accelerated solvent extraction system (ASE) with low solvent consumption, (ii) an automated turbovap evaporating system, (iii) a five-point automated calibration method, (iv) an isotope-dilution method which inherently tracks and corrects for method recovery during all steps of sample preparation and analysis for all PAH, and (v) an automatic quantification/reporting method which also tracks quality control data.

Additional quality control/quality assurance (QA/QC) measures have been adopted using the multi-point calibration method, including: a) the tracking of instrumental performance for relative response factors (RRF's) of quantitation standards versus native PAH in a continuing calibration method, b) tracking of calibration curve linearity, c) analyte recovery corrections via isotope-dilution quantification, and d) greater quantification accuracy due to closeness in chemical structure/behavior of isotopic analogues of the target PAH. Quantification of 2 new PAH (benzo[e]pyrene and perylene) was incorporated. Substantial cost savings have been achieved as a result of in-house preparation of the individual PAH standard solutions and PAH mixtures used as quantification/recovery standards and calibration standards.

Charts A and B show a comparison of the within-run percentage recovery of PAH achieved using the old method (PSAPAH E3350) versus the new method (PSAPAH E3425). Analysis of a fortified blank soil matrix (n=10) as illustrated in Chart A, shows that the range of PAH recoveries has narrowed and improved from 61 - 105% (method E3350 - dark grey bars) to 92 - 119% (new method E3425 - light grey bars). The precision of the PAH determinations has also improved (expressed as percentage relative standard deviation in the error bars) from a range of 4.5 - 19 %RSD to 1.0 - 7.7% using the new method. Analysis of a certified sediment reference material (EC-3, produced by the National Water Research Institute) as illustrated in Chart B has yielded similar improvements in accuracy from 58 - 69 % recovery of certified PAH to 88 - 117 % recovery using this new isotope dilution method.





This new method was adopted for its speed, simplicity, reduction in sample handling, savings in labour, equipment and bench space and low solvent requirements. As a result of the use of these automated extraction and evaporation systems and the elimination of several sample dilution/transfer/handling steps, this new method

PSAPAH-3425 has resulted in a sample preparation that consumes 3 - 4 times less solvent in less than half the preparation time. Overall, the adoption of automated extraction and evaporation systems and the use of isotope-dilution quantification and multi-point calibration in the new method has improved the precision and accuracy of PAH data produced and has largely reduced the time required for sample preparation and analysis.

Current Status

The new method has been completed and an internal Quality Management Unit (QMU) audit has been performed.

III. Evaluation of Analytical Methods to Support the Toxicity Characteristic Leaching Procedure (TCLP)

Study Leader:	John Carron [Physical Chemistry & Litigation Section]
Customer:	Standards Development Branch/Waste Management

Objective

To develop a standard method for the generation of leachates, and their subsequent analysis, to support the Toxicity Characteristic Leaching Procedure (TCLP).

Background

A regulation to amend Ontario Regulation 347 came into effect 31 March, 2001, known as Ontario Regulation 558–00. This Regulation lists an extensive group of analytes that must be monitored in leachate samples to determine whether the corresponding solids can be classified as "Hazardous Waste" under the Regulation. A

leaching procedure developed by the US Environmental Protection Agency (USEPA), known as the Toxicity Characteristic Leaching Procedure (TCLP), was adapted for Ministry of Environment use. Analysis of the leachates is challenging, because the 88 analytes designated under the Ontario Regulation includes organic and inorganic compounds that have widely varying chemical & physical properties.

Results

Because the organic analytes include both volatile and semi-volatile compounds, leachates for testing were generated by both an apparatus known as a "zero headspace extractor" (ZHE), and by using a standard mechanical mixing method. In a series of studies, the suitability of the ZHE and of mechanical mixing to provide suitable leachates for analysis was evaluated by spiking extraction fluids and real-matrix samples after extraction. Acceptable performance was set at a minimum 50% spike recovery and 50% relative standard deviation (%RSD). Several custom spiking solutions, prepared by Protocol Analytical Supplies Inc., were required, because of the large number of analytes to be tested, and the different concentration ranges needed.

Overall, the spiking studies indicated good results for most analytes, including volatile organics (vinyl chloride and methyl ethyl ketone were not studied), metals, and most semi-volatile organics. In the worst case scenario, recoveries of several chlorinated pesticides were below 50%, and the benzo[a]pyrene recovery was about 10%. Although more work is required to study the poor performance of a few isolated analytes, the overall recoveries and precision show that the methods developed are acceptable for routine use. In practice, an initial bulk analysis is recommended to screen samples for volatiles in waste samples. If volatiles are detected, then the ZHE is used.

During the investigation of a large number of waste samples, one was found that seemed suitable for use as a reference material for metals. A quantity of this material was processed as a certified reference material (CRM) and is being evaluated by a round-robin study.

Current Status

The leaching procedures are documented as a standard MOE–LSB method. Further work is underway to investigate the poor recoveries of a few analytes. Analysis of the leachates is currently being performed by using several existing MOE–LSB methods, and additional work is underway to simplify the analysis procedures to allow for more analytes to be determined in fewer analytical runs.

IV. Study of Freeze–Drying to Improve Detection Limits for Chloroorganics in Biota

Study Leader:	Eric Reiner [Dioxin & Toxic Organics Section]
Study Team:	Laila Fayez, Corina Lucaciu
Customer:	Al Hayton, Environmental Monitoring & Reporting Branch

Objective

To improve detection limits for organochlorine pesticides, PCBs, Toxaphene, Dioxins/Furans and other related compounds by up to 10 times.

Background

Freeze drying of biota removes water and effectively concentrates the sample matrix by up to 10 times. Non-volatile organic compounds will therefore be concentrated with respect to undried biota. The freeze drying process also breaks up cell walls and allow the sample to be extracted without acid digestion. The samples are extracted using Accelerated Solvent Extraction (ASE). Extracts are cleaned using standards Florisil, silica, alumina and/or activated carbon cleanup columns.

Results

The method is currently being validated using a set of 10 Chinook salmon samples from the Credit River. Each of the 10 samples will be analyzed 3 different ways: wet weight / acid digestion, freeze dried / acid digestion, freeze dried ASE extraction. About 500 - 600 grams of ground dorsal fillet of 10 different Chinook samples were obtained. Each of the 10 samples were split in half and one of the halves were freezed dried for until there was no additional loss of weight. Samples have been prepared and analyzed for dioxins, furans and DLPCBs for the wet and freeze dried samples using the acid digestion procedure.

Current Status

The ASE samples must still be analyzed.

V. Determination of Brominated Diphenyl Ethers

Study Leader:	Karen MacPherson [Dioxin & Toxic Organics Section]
Study Team:	Terry Kolic, Eric Reiner
Customer:	Environmental Monitoring & Reporting Branch, Standards Development Branch

Objective

To develop an isotope dilution method for the determination of Brominated Diphenyl Ethers in environmental samples at the pg/g to ng/g level.

Background

The use of Brominated Flame Retardants (BFRs) and resulting levels of associated contaminants in the environment have increased steadily since the 1980s. Materials treated with BFRs, including fabrics, furniture and computer equipment

reduce injuries and deaths due to fire, however, releases into the environment and degradation of these products may result in human exposure, which can lead to a number of health effects including: thyroid hormone disruption, neurodevelopment deficits and cancer for some congeners. BDEs are bioaccumulative and a select number of congeners appear to be very stable in the environment. Significant levels of BDEs have been detected in sewage and sewage sludge. Application of BDE containing sewage sludge can result in accumulation of these compounds due to repeat application on agricultural fields. Over a number of years, background levels may exceed recommended levels and guidelines.

The analysis of BDEs is challenging. This group of brominated compounds has a very broad range of physical and chemical properties that makes the analysis of all congeners in a single analytical run quite difficult. Melting points range from <0°C penta or lower (Br $\leq$ 5) to over 300°C for decabromodiphenyl ether. Many congeners are also very thermally labile and decompose before they reach their boiling point, making analytical separation and detection very difficult. Analysis by gas chromatography provides the best possible separation of congeners for analysis. High resolution mass spectrometry (HRMS) with positive electron ionization provides the best selectivity and sensitivity. HRMS can meet mass range detection requirements, however, finding reliable and clean calibrant gases (e.g. PFK) for the upper mass range can be difficult.

Results

Analytical conditions for the detection of tetra to hepta BDE congeners have been established. Reproducible detection and quantification of the decabromo congener (BDE209), a major component in solid matrices such as sediments, soil and sludges, has proven to be a significant challenge because of its high mass (960 daltons). It is also thermally labile and has a very high melting point (325 °C). These properties require very specific injection and chromatographic conditions to ensure analyte decomposition does not occur during the analytical process. The injection system has been modified with a Restek "Uniliner". The Uniliner modifies the GC injection port to an on-column type injector and allows the injector temperature to be lowered. This reduces decomposition of BDE209 in the injector and enables it to be transferred quantitatively to the GC column. Other studies included the preliminary investigation of a high temperature chromatographic carborane phase (RTX-500). This phase is very stable and can stand oven temperatures of over 380°C. The RTX-500

column has similar chromatographic properties to the standard 5% phenyl (RTX-5, DB-5) phase and allows for much faster ramp rates to higher final temperatures reducing column residence times for labile congeners. RTX-500 also produces chromatographic patterns that are slightly different from 5% phenyl columns which may result in fewer or different co-eluting pairs and interferences.

Current Status

Method conditions for most congeners are set. Method validation with round robins, spiked matrix samples and certified reference materials is still needed. At the present time, the composition of analytical standards has not obtain final consensus among the analytical community and different jurisdictions.

Future work will involve:

- ❑ Final consensus on composition and completion of a new series of calibration standards for isotope dilution quantification to include environmentally important congeners.
- ❑ Collaborative work with Environment Canada and USEPA to finalize and validate a reference method that will be included in the USEPA GC/HRMS 1600 series.
- ❑ Collaborative work with OMAFRA and Environment Canada to complete a study to assess the levels of BDEs in a variety of solid environmental matrices focussing on sludge and land applied sludge.
- ❑ Investigation of the extent of contamination of BDEs in Great Lakes fish.

VI. Congener-Specific Toxaphene Determination

Study Leader:	Gerry Ladwig [Dioxin & Toxic Organics Section]
Study Team:	Tony Chen, Eric Reiner
Customer:	Alan Hayton [Environmental Monitoring & Reporting Branch]

Objective

To develop a method for the determination of toxic toxaphene congeners in environmental samples.

Background

Toxaphene is a complex mixture of polychorinated bornanes and camphenes that was extensively used as a pesticide and piscecide. There are more than 30,000 possible congeners, but the technical mixture typically contains about 600. Out of this group there are 22 that are considered toxic.

Results

Standards containing the 22 toxic congeners were obtained from 2 separate suppliers. A series of standards and Performance Evaluation (PE) samples were analysed for the toxic congeners by using dual column gas chromatography (GC) with electron capture (ECD) detection. Initial results produced data in which a number of congeners were biased high or where false positives were detected. A negative chemical ionization GC/MS method using microbore GC columns is being investigated to determine if interferences can be eliminated using this more selective analytical technique.

Current Status

Initial results using the 20M 0.1mm id, 0.1 um film 5% phenyl column which contains almost twice as many theoretical plates as the standard 30M [0.25mm id, 0.25 um film] columns show that the microbore columns separate more than 22 components (up to 25) in the standard mixes. The components in these standards mixes need to identified and confirmed and method validation needs to be completed.

VII. Determination of Polychlorinated Naphthalenes

Study Leader:	Karen MacPherson [Dioxin & Toxic Organics Section]
Study Team:	Vin Khurana and Eric Reiner; Chris Marvin [National Water Research Institute]
Customer:	Environmental Monitoring and Reporting Branch, Standards Development Branch

Objective

To develop an isotope dilution quantification method for analyses of various PCN congeners in environmental samples with focus on Dioxin-like PCN congeners.

Background

Polychlorinated naphthalenes (PCNs) were first manufactured for use as flame retardants and dielectric fluids in the early 1900s. During WWI their use increased as flame retardants to protect paper and fabrics. After the war, PCNs were also used as cutting oils, engine oil additives, electroplating stop-off compounds, in diecasting, ship insulation, wood/fabric and paper preservatives. After WWII, because of health related problems in factory workers, and with the arrival of plastic substitutes for insulation and Polychlorinated Biphenyls (PCBs), the production of PCNs began to decline. PCNs have similar chemical and physical properties to PCBs and Dioxins. However, unlike Dioxins/Furans and PCBs there is little information on PCNs regarding amount of world-wide production, toxicity, sources, environmental levels, fate and transport.

Today, a growing recognition of worldwide distribution of PCBs, has renewed research interest in the toxicity and fate of PCNs. There is evidence that some of the 75 PCN congeners are commonly found in living organisms and are persistent in the environment. Although these compounds have not yet been identified for international regulation, unlike many other chlorinated Persistent Organic Pollutants (POPs), Toxicity Equivalence Factors(TEFs) have recently (2000) been proposed for several PCN congeners which have shown Dioxin-Like toxicity (bind to Ah receptor).

A preliminary investigation of suspended sediment samples from the Detroit River were analyzed to determine the spatial distributions of contaminants including

polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs), dioxin-like PCBs (DLPCBs) and PCNs. The Detroit River is one of the four major connecting channels in the Great Lakes Basin, providing the link between western Lake Erie and Lake St. Clair. The highly urbanized and industrialized watershed represents a variety of sources of chemical contaminants to the river, including urban runoff, sewage treatment plant effluents, combined sewer overflows and industrial wastes. Results of this investigation support the need for further research with regards to environmental occurrence, impact and fate of PCNs. Furthermore, spatial distribution and suspended sediment quality can be used as a benchmark to assess toxicity and the potential for remediation of sites containing contaminated sediment.

Results

The spatial distribution of PCN contamination was somewhat different to that of PCDDs/PCDFs and DLPCBs, with the highest level of total PCNs (8,200 ng/g) detected at a site in the Trenton Channel near Elizabeth Park; TEQs for PCNs in the Trenton Channel ranged from 73 pg/g to 3,300 pg/g. The data indicate that PCNs represent the major contribution to dioxin-like biological activity in Detroit River suspended sediments. External standard quantification techniques were used to determine PCN concentrations for this study.

Current Status

A set of ^{13}C-labelled standards containing environmentally significant and dioxin-like PCNs have been obtained. A set of comprehensive standards including a calibration series, labelled fortification standards, injection standards and native (unlabelled) standards will be prepared to complete development of a congener specific isotope dilution method for the determination of PCNs in biota and sediment/soil.

Publications

1. Marvin, C.H., Alaee, M., Painter, S., Charlton, M.N., Kauss, P., Kolic, T., MacPherson, K., Takeuchi, D. and Reiner, E.J.; Persistent organic pollutants in Detroit River suspended sediments: Polychlorinated dibenzo-p-dioxins and dibenzofurans, dioxin-like polychlorinated biphenyls and polychlorinated naphthalenes. Submitted to Chemosphere (2002).

VIII. GC/MS Determination of 3-chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone in Drinking Water - Results of Field Study

Study Leader: Paul Yang [Applied Chromatography Section]
Study Team: Larry Matchuk, Franka Morra, Chunyan Hao, Lorna Grey
Customer: Drinking Water Coordination Committee [SDB & EMRB] and D. Dobrin [Operations Division]

Objective

To validate the new MX method using field samples collected from various water treatment plants for the monitoring of the chlorine disinfection byproduct, including (DBP) 3-chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone (MX).

Background

The chlorination of organic substances present in water systems has resulted in the production of numerous DBPs, but many have yet to be identified. Some, such as the trihalomethanes (THMs), are known to be carcinogenic to laboratory mammals, although at doses far greater than human intakes from drinking water. The compound 3-chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone (MX) was shown to be genotoxic in the Ames test (a bacterial system). In fact, the MX concentration in samples accounted for about 30% of the previously unexplained total genotoxicity of extracted DBPs. The Applied Chromatography Section (AC) previously developed a method for the analysis of MX, and carried out a 3-month field study during 2001. We document here major findings from this study and discuss the future development work required to bring this analytical method on-line.

Results

Using methods E3383 (haloacetic acids), E3400 (CB/OC/PCB), and the newly developed MX method, we analyzed a total of 324 samples collected from 9 water treatment plants (raw, treated, distribution) over a 12-week period. Analytical data were

compiled for treated water and are shown in the Table below for six of the nine WTPs. We also include water quality data, especially Cl_2 concentrations, for comparison.

WTP	pH	Total Cl_2 (mg/L)	Post Cl_2 (mg/L)	HCCPD (ng/L)	Dalapon, (µg/L)
#1	7.34	1.37	3.59	39	0.78
	8.1	1.33	3.41	33	<.20
	6.71	0.97	4.64	16	<.20
	7.02	1.53		28	0.42
	6.63	1.19	2.31	33	0.48
	7.19	1.32	5.28	65	0.38
	7.16	1.25	3.73	44	0.7
	6.87	1.57	2.96	104	0.45
#2	7.47	1	1.4	ND	<.20
	7.48	1	1.5	ND	<.20
	7.48	1	1.23	ND	<.20
	7.48	1	0.99	ND	<.20
	7.46	1	1.3	ND	<.20
	7.49	1	1.4	ND	<.20
	7.46	1	1.14	ND	<.20
#3	6.91	2.88	7.5	38	1.93
	6.89	2.91	6.5	60	1.94
	6.87	3.23	3.3	59	1.78
	6.95	2.18	4.9	49	1.25
	7.17	2.32	4.9	49	0.98
	7.16	2.52	4.9	29	1.1
	7.26	2.01	4.9	29	0.81
	7.18	2.29	4.9	53	0.67
#4	6.7	2.12	3.97	28	0.75
	6.6	1.84	4.2	28	0.48
	6.7	2.68	4.14	36	0.71
	6.7	2	3.76	36	0.7
	6.8	1.83	3.03	21	0.57
	6.8	2.38	3.4	27	0.8
#5	7	1.74	2.8	27	0.38
	7.1	1.82	2.7	38	0.48
	7.22	1.27	5.1	18	0.44
	7.26	1.43	4.37	24	<.20
	7.15	1.3	5.76	ND	0.42
	7.1	1.57	5.12	20	0.48
	7.15	1.23	5.23	16	0.3
	7.4	1.4	4.09	17	0.41
	7.1	1.5	3.76	23	0.47
#6	7.24	1.49	2.5	101	0.9
	7.19	1.05	2.5	130	0.71
	7	1.54	2.5	280	0.74
	7.07	1.17	2.5	121	0.66
	7.23	1.22	2.5	164	0.46
	7.17	1.29	2.5	145	0.44

HCCPD: Hexachlorocyclopentidene; WTP: Water Treatment Plant

We would like to note that no MX was detected during this study, at current detection limits (5 ppb). According to other studies reported after this investigation, MX was detected in treated water at 16 to 125 ppt. At least 1L sample sizes would be required for the method reported here to detect MX at these concentrations. Therefore, the section is in the process of developing a SPE method which will help achieve a much lower detection level for the compound MX.

The current study did validate the assumption that Dalapon and/or HCCPD did not exist in any of the raw water samples. There is, however, a definite correlation between the amount of Dalapon and/or HCCPD detected and chlorine and pH of the water. In treated water samples with no observable chlorine and a neutral pH, there is no production of Dalapon or HCCPD. At the higher chlorine values and lower pH of the water samples, more Dalapon and HCCPD are produced. There is a threshold (i.e., with chlorine at less than 1 mg/L), where formation of HCCD and Dalapon are reduced. We also observed that in WTPs using sodium hypochlorite for post chlorination instead of chlorine, a lower level of both Dalapon and HCCPD were found.

Current Status

The MX study confirmed for the OD that Dalapon, also classified as a pesticide, is not a concern when present in treated water with high chlorine, low pH, and is not in the corresponding raw water. A SPE procedure has been developed for the preparation of MX from 1-L water sample. Analytical methods are being re-investigated for the possible decomposition of MX standards during storage.

IX. Isolation, Detection & Enumeration of Salmonellae in Biosolids

Study Leader:	Rhonda Schop [General Chem. & Microbiology Section]
Study Team:	Paul Vyse, Janet Chow
Customer:	Standards Development Branch, SWAT

Objective

To develop a method for isolating and quantifying the concentration (per g) of *Salmonella sp.* in treated Biosolids. These measurements will be used to evaluate the pathogenic risk due to Salmonella sp. upon application of Biosolids to land.

Background

The US EPA has developed a standard for Salmonella sp. in Type A Biosolids for land application. MOE is currently reviewing application of biosolids for land application and corresponding certificate of approvals. This method was adapted from a standardized method for detection and enumeration of *Salmonella sp.* in food.

Results

Using a Most Probable Method (MPN), a statistical estimation of the concentration of Salmonella sp. was determined on a per gram (wet weight) basis. Evaluation of biosolids from various degrees of treatment (from raw to final treatment) was conducted. It was determined that the minimum detection limit was found to be <3 per gram. High reproducibility of results was obtained with this method and good recovery using spiked samples was also determined.

Current Status

This project is nearing completion. The method E3433 (Isolation, Detection and Enumeration of Salmonellae in Biosolids) has been written and is currently undergoing a procedural audit.

X. Isolation & Enumeration of Clostridium perfringens in Biosolids

Study Leader:	Rhonda Schop [General Chem. & Microbiology Section]
Study Team:	Paul Vyse, Janet Chow
Customer:	Standards Development Branch, SWAT

Objective

To develop a method for isolating and quantifying the concentration (per g) of *Clostridium perfringens* in treated Biosolids. These measurements will be used to evaluate the pathogenic risk due to *Clostridium perfringens* with land application of Biosolids.

Background

Enumeration of *Clostridium perfringens* and other spore-forming bacteria in treated material (including biosolids) assists in evaluating the effectiveness of treatment prior to land application. MOE is currently reviewing application of biosolids for land application and corresponding Certificate of Approvals.

Results

Inoculating selective bacteriological agar and specific biochemical confirmation tests, confirmed concentration of *Clostridium perfringens* was determined on a per gram (wet weight) basis. Evaluation of biosolids from various degrees of treatment (from raw to final treatment) was conducted.

Current Status

This project is nearing completion. The method (no method code) (Isolation and Enumeration of *Clostridium perfringens* in Biosolids) is currently being written and minimum detection limits are being evaluated.

C. Analytical Reference Activities

The broader focus of this section is intended to capture the wide range of significant activities, in addition to collaborative projects with outside groups, that the Laboratory Services Branch performs. The majority of these activities involve development and evaluation of commercial instrumentation or products, external laboratory evaluations and assistance, and communication/technology transfer actions.

I. Evaluation of GC and HPLC Columns for Organic Analytes Determination

LSB Study Team:	Paul Yang [Applied Chromatography Section] – projects #1, #2; Karen MacPherson, Eric Reiner [Dioxin & Toxic Organics Section] – project #3
Collaboration with:	Valco Instruments Inc. [#1, #2]; Restek Corporation, Bellefonte, PA [#3]

1. GC Column. Working with Dr. Rob Wohleb of Vici Valco (Gig Harbor, WA), GC columns of various physical parameters and β (film thickness) were evaluated for TOF-MS based analysis. The goal was to optimize the nHETP and column capacity, and minimize GC column bleed to achieve the best price/performance ratio for a general purpose fast GC/TOF-MS analysis. Using validation data obtained from Methods E3400 (OC/CB/PCB) and E3399 (PAH), we eliminated the 0.1- and 0.25-mm i.d. columns and investigated better performing columns with i.d. in the 0.18- to 0.15-mm range.

2. LC Column. Various column were evaluated for the ability to baseline separate two coeluting carbamates, aldicarb and carbofuran, for enhanced price/performance ratio, instrument sensitivity, and savings from the use of a much smaller amount of mobile phase. This will also lead to significant improvements in sample identification that will be beneficial to all environmental laboratories. Currently, we can achieve about 25% of FWHH separation and are

working toward to achieve the same as that can be offered by a benchmark column.

3. Determination of an Analyte-Specific Column for Dioxin-like Compounds. The analysis of polychlorinated dioxins and furans requires up to four of the 17 toxic congeners to be uniquely confirmed on at least two separate column phases. At the present time, there is no column (stationary phase) that can separate all of the 17 toxic dioxin/furan and 12 dioxin-like PCBs (DLPCBs) in a single analysis. This project was undertaken to review a number of different column phases in order to produce an analyte-specific column for dioxins, furans and DLPCBs. An analyte specific column can significantly reduce analysis times and increase instrument capacity. This was accomplished previously with the Organochlorine Pesticides. DTO completed the final testing for the Restek CLPesticides columns and subsequently modified the method to Fast GC method using 0.18mm, 0.14 m columns. Run times for OC pesticides were reduced to under 10 min. from 55 min using the analyte-specific columns.

A number of different dioxin/furan and PCB standards were run on 6 different phases: Rtx-1, Rtx-5, Rtx-500, Rtx-VRX, CLPestcides-2 and an unidentified experimental phase. Data (retention times and coeluting pairs) from these standards will be placed ion an ab initio calculation routine in order to identify the optimal stationary phase composition. Elution order of a number of congeners changed significantly with the varying phases. This implies that a combination of a subset of the phases listed above should be able to uniquely separate all congeners.

The Rtx-500 exhibited very low column bleed. This high temperature phase was also used to analyse the brominated diphenyl ethers using a modified injection liner (uniliner). The uniliner converts a standard split/splitless injection port to an on column type injector. Considerably greater sensitivity was observed for the decabromo diphenyl ether using the Rtx-500 column with a uniliner injector.

II. Development of Environmental Reference Materials

LSB Study Team:	Sathi Selliah [Quality Management Unit]; Eric Reiner [Dioxin & Toxic Organics Section]
Collaboration with:	Brock Chittim [Wellington Laboratories]

A freeze-dried fish reference material developed last year was distributed by Wellington Laboratories in a round-robin study to generate consensus concentration values of selected analytes. This year a pilot project to produce vegetation reference material for organic parameters was undertaken. The results obtained so far have been very promising, especially for chlorinated dioxins/dibenzofurans (PCDDs/PCDFs) and the dioxin-like PCBs (DL-PCBs). This material was used to help evaluate an external overseas laboratory.

III. Mass Spectrometry Discussion Group

LSB Leader:	Vince Taguchi [Mass Spectrometry Section]
Collaboration with:	Toronto Area Mass Spectrometry Discussion Group

The Laboratory Services Branch (LSB) supports communication activities between analytical professional in Ontario. For the past few years, LSB has been the site of the regular meetings of the *Toronto Area Mass Spectrometry Discussion Group*. Organized by Dr. Vince Taguchi, six evening seminars were held during 2001 in the 125 Resources Road auditorium. The distinguished lineup of speakers and their topics of discussion were:

- Dr. Alexandre A. Shvartsburg, York University. *Using Ion Mobility Spectrometry to Analyze the Composition and Illuminate the Chemistry in the Gas Phase* [January 25].
- Dr. Gary Paul, Thermo Finnigan. *New Instrumentation and Applications: High Resolution Benchtop Triple Quadrupole Mass Spectrometer* [February 22].
- Dr. Richard W. Smith, Agilent Technologies. *LC/MS and LC/MS/MS with an Ion Trap: Recent Developments* [April 10].
- Dr. Nick Karellas, Ministry of the Environment. *Mobile Air Monitoring: The Saga of the TAGA* [May 16].

- ❑ Dr. Heather Gamble, Unisearch Associates Inc. *Environmental Monitoring using Tunable Diode Laser Technology* [October 3]. (Seminar co-sponsored by Sprctroscopy Society of Canada)
- ❑ Professor Diethard K. Bohme, York University. *Flow-Tube Mass Spectrometry: Applications and Developments* [November 13].

For notices of upcoming seminars, those interested should check the internet site: www.csms.inter.ab.ca

IV. Technology Evaluation Studies

LSB Leader:	Gerry Ladwig [Dioxin & Toxic Organics Section]; Ernie Chen, Barry Ali, and Paul Yang [Applied Chromatography Section]
Collaboration with:	Gordon McFarlane [Valco Instruments];

1. Horizon Technology Automated SPE Extraction Station. Two models of Horizon Technology SPE stations (4770 and 4790) were compared side-by-side for the extraction efficiency of triazine pesticides. Results showed that 4770 is a better model in terms of simple of operation, sample turnaround time, and cost of SPE cartridges. The results were presented at the 23rd Annual Pesticide analysis conference.

V. International Round-Robin Studies

LSB Leader:	Sylvia Cussion [Quality Management Unit]
Collaboration with:	various

A critical activity to benchmark laboratory performance against that of other international leaders, and to enhance an internal QA program, is activity in external round-robin studies. In the past year, LSB has participated in 39 such studies. International studies included one CRM certification study from the Laboratory of the Government Chemist (LGC) in the UK, for PCB Congeners in Sewage Sludge. The General Chemistry and Microbiology Section and Spectroscopy Section participated in

two different studies from Norway (water and precipitation sample types), and four studies from the National Authority for Testing in Australia (NATA), also in water. Dioxins and dibenzofurans in fly ash for the Second study originating in Italy were determined by using MOE Method E3418 (Dioxin & Toxic Organics Section – DTO). In addition, the DTO Section participated in the 7th round-robin for soil and flyash samples from Umeå University (Sweden). New for 2001 was the participation in a study for Brominated Diphenyl Ethers in soil and fish, organized by Quasimeme in the UK.

VI. Analytical Reference Assistance

LSB Leaders:	various
Collaboration with:	various

1. CAEAL Assessors. LSB provides staff who act as assessors for the Canadian Association for Environmental Analytical Laboratories (CAEAL). In 2001, the certified assessors who performed this service were Cathy Doehler, Ann Jones, Dallas Takeuchi, and Rhonda Schop.

2. NDMA Determination. Because the Mass Spectrometry (MS) Section developed a reference method for NDMA, they are sometimes consulted by other laboratories for analytical assistance and conflict resolution for this difficult determination. In 2001, the MS Section assisted various water treatment plants in investigating several cases of incongruent results for NDMA reported by private contract laboratories. Vince Taguchi of the MS Section also served on a committee set up by the State of California to review research proposals to develop a low-cost NDMA method.

3. Environment Canada Collaboration. The Dioxin and Toxic Organics Section is involved in a series of ongoing studies with Environment Canada to investigate trends in dioxin-like compounds in sediments & biota of the Great Lakes. These studies include the following: *I. Great Lakes Sediment Assessment Program.* The Ontario Ministry of the Environment is a key partner in an Environment Canada-led team mandated with long-term research and monitoring of environmental conditions in the Great Lakes, including the presence of persistent organic pollutants (POPs) that can adversely impact wildlife, biodiversity and

aquatic ecosystems. Comparison of current levels of POPs with historical information has allowed the determination of temporal trends, and the degree of improvement in environmental quality since the advent of measures to reduce discharges. *II. Persistent Organic Pollutants Associated with Suspended Sediments in Great Lakes Areas of Concern.* This is a five-year program to monitor the distribution, sources and fate of POPs in Great Lakes Areas of Concern (AOCs). Studies are being carried out in the corridor extending from the Detroit River through Lake St. Clair and the St. Clair River, and in Hamilton Harbour. This information has provided the Agencies, Remedial Action Plans (RAPs), and Lake Area Management Plans (LaMPs) with current knowledge on levels and distributions of contaminants in AOCs and are a benchmark in assessing ongoing remediation of severely contaminated sites which are significant sources of POPs to open-lake. *III. Investigation of Impacts of Exotic Mussels (Dreissena) on Contaminant Cycling in the Lower Great Lakes.* The Ontario Ministry of the Environment has participated in a joint program with Environment Canada to assess the potential impacts of zebra mussels on contaminant cycling in nearshore areas of the Great Lakes. These impacts are assessed through comparison of levels of POPs in sediment extensively colonized by mussels, with sediments in proximity that are not colonized but are exposed to similar environmental conditions. This work has clearly demonstrated the ability of these exotic mussels to influence the chemical and physical nature of benthic environments they colonize, and has identified a heretofore largely unrecognized vector for transfer of contaminants through the benthic and detrital food chains to higher trophic levels.

VII. Conference, Education and Outreach Activities

LSB Leader:	Ray Clement [Director's Office]
Collaboration with:	various

1. 47th ICASS Conference. The 47th International Conference on Analytical Sciences and Spectroscopy (47th ICASS) was held in Toronto August 20-22, 2001. This meeting is the annual conference of the Spectroscopy Society of Canada, and was chaired by Ray Clement of LSB. Other LSB staff who

organized sessions were Eric Reiner, Paul Yang, and Vince Taguchi. In addition, LSB staff prepared several presentations (see list below).

2. Student Lectures. Various LSB staff were invited to give presentations to College or University classes regarding special topics in environmental analytical chemistry, laboratory careers, and related issues. During 2001, presentations were made to students at the University of Guelph, University of Toronto, and the University of Western Ontario.

3. Scientific Publication Support. LSB staff served on several editorial boards for scientific journals, and several staff assisted journals by providing reviews of technical manuscripts submitted for publication. A partial list of journals served includes: Chemosphere, Environmental Science & Technology, and the Canadian Journal of Analytical Sciences and Spectroscopy. In addition, some staff were asked to review grant proposals submitted to the Natural Sciences and Engineering Research Council of Canada (NSERC).

4. Science Teachers' Association of Ontario (STAO). STAO publishes a science magazine five times each year, called *The Crucible*. The *Crucible* publication committee in 2001 was chaired by Ray Clement of LSB. The committee solicits articles, reviews all submissions for quality and appropriateness, and proofs each issue before it is sent for printing.

5. Job Shadowing. Adrienne Boden job shadowed a student from Seneca College and demonstrated the operation of the HRMS for dioxin analysis on October 15th, 2001.

6. Aventis Biotechnology Challenge. Ray Clement chaired the panel of Judges who evaluated student posters prepared for the Aventis biotechnology competition held May 1, 2001, at the Ontario Science Centre.

D. LSB Seminar Series

Eight seminars were organized in 2001. They ranged from small, specialty topics to more mainstream topics of wide interest. The topis allowed for excellent training opportunities, and also to introduce technical staff to developing technologies that could have significant impact to the environmental analytical field in future years. Seminars were well attended by not only LSB staff, but also by staff of the Ministry of Health and from external organizations. Brief descriptions of the seminars held are given below.

I. Comprehensive GC Seminar: Rick Parmely and Gary Stidsen, Restek Corporation [hosted by MOE-LSB and Chromatographic Specialties Inc.]

This full-day event was attended by 69 people on February 15, the majority of whom were from private-sector organizations. Seminar participants received an excellent introduction to practical GC use, including column installation, maintenance, and troubleshooting. Applications in several fields, with specific emphasis on environmental, were discussed.

II. New Technology for Rapid Testing of Microbiological Parameters for Environment and Health; Peter Lea, Umedik Inc.

On March 27, about 60 attendees learned about new developments in the use of "lab on a chip" technology for microbiology parameter testing. Dr. Lea described the development of a biochip that performs "on the chip" separation of fine particles from the sample fluid, after which multiple biochemical analyses can be performed. This technology was used to screen Walkerton samples with excellent results.

III. Identification and Quantification of Semivolatiles, Volatiles, and Herbicides in Environmental Samples Utilizing Dual-PDHID Detectors; Martin Okiro, Valco Instruments Inc.

A seminar was presented to eight staff on May 24 concerning recent environmental applications of Valco's new technology *Pulsed Discharge Helium Ionization Detector*. This detector is a possible replacement of the conventional Electron Capture (ECD) detector, but is versatile enough to be used for a much greater range of environmental applications. This detector has been under evaluation at LSB over the past year.

IV. A New Generation of HPLC Columns to Reduce Analysis Time; Nicola Jones, Hichrom Ltd. [hosted by MOE-LSB and Canadian Life Sciences]

This presentation gave 15 LSB staff an insight into the latest developments in the field of High Performance Liquid Chromatography (HPLC). In recent years, significant improvements have been made in the quality of the bonded silica particles used to manufacture HPLC columns, and in stationary phase bonding and column packing techniques. Consequently, there has been rapid growth in the number and type of HPLC columns available. The seminar was presented on June 25.

V. Improved Productivity for Organic Analysis Sample Preparation (EPA 500/600/8000 Series Methods); Mark Lessard, Horizon Technology

Dr. Lessard discussed the benefits of automating the Solid-Phase Extraction (SPE) procedure to improve sample productivity for aqueous sample analysis. Data that illustrated the precision, accuracy, and analyte recoveries from application of SPE to EPA-series methods were presented. Dr. Lessard then performed a cost analysis that compared manual extraction and automated SPE techniques. Thirty-three LSB staff attended this seminar on June 27.

VI. Solid Phase Extraction: Principles & Recent Developments; Robert Molino, Varian Canada Inc.

In this presentation a review of basic principles of Solid Phase Extraction (SPE), recent developments in polymer sorbents, and automated method development was presented to 13 LSB staff. The importance of sample preparation, solid supported liquid/liquid extraction, and general SPE methodology was highlighted. This seminar was presented July 18.

VII. Technical Overview of Pulsed Discharge GC Detector; Huamin Cai, Valco Instruments Inc.

This seminar, delivered on August 14 to 15 LSB staff was a follow-up to a seminar delivered on May 24 (see III, above). Whereas the previous seminar emphasized applications of the pulsed discharge GC detector, this one presented an overview of the technology and basic principles of operation. The seminar leader, Dr. Cai, is one of the leaders in the development of this relatively new technology.

VIII. Environmental Analysis Using HPLC & LC/MS; Joe Romano, Waters Ltd.

This half-day seminar was held September 20, in which 23 LSB staff participated. The fundamentals of HPLC were stressed, with specific emphasis on environmental analysis applications. Recent advances in solvent delivery, interface technology, sample preparation, and column chemistry were discussed. The seminar provided the basic knowledge to understand when and where to use HPLC and/or LC/MS to full advantage for environmental analysis.

E. Publications, Presentations & Staff Recognition Laboratory Services Branch

A. Publications

1. S.S. Selliah, S. Cussion, K.A. MacPherson, E.J. Reiner and D. Toner. Development of a reference material for routine performance monitoring of methods measuring polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and dioxin-like polychlorinated biphenyls. *Fresenius J. Anal. Chem.* **2001**, *370*, 208-212.

2. Vince Y. Taguchi. Structural elucidation of disinfection by-products in treated drinking water. *Rapid Communications in Mass Spectrometry* **2001**, *15*, 455-461.

3. Patrick W. Crozier, Jeffry B. Plomley and Larry Matchuk. Trace level analysis of polycyclic aromatic hydrocarbons in surface waters by solid phase extraction (SPE) and gas chromatography–ion trap mass spectrometry (GC–ITMS). *Analyst* **2001**, *126*, 1974-1979.

4. Lorna Grey, Bick Nguyen and Paul Yang. Liquid chromatography/electrospray ionization/isotopic dilution mass spectrometry analysis of *n*-(phosphonomethyl) glycine and mass spectrometry analysis of aminomethyl phosphonic acid in environmental water and vegetation matrixes. *AOAC International* **2001**, *84*, 1770-1780.

5. Ray E. Clement, Paul W. Yang and Carolyn J. Koester. Environmental analysis. *Anal. Chem.* **2001**, *73*, 2761-2790.

6. K.A. MacPherson, E.J. Reiner and T.M. Kolic. Dual microbore column GC/HRMS analysis of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DLPCBs). *Proceedings of 21st International Symposium on Halogenated Environmental Organic Pollutants and Persistent Organic Pollutants (POPs)*: Jae-Ho Yang, editor, **2001**, *50*, 40-44.

7. T.M. Kolic and E.J. Reiner. An investigation of Aroclor Mixtures and their dioxin-like PCB (DLPCB) congener contributions. *Proceedings of 21st International Symposium on Halogenated Environmental Organic Pollutants and Persistent Organic Pollutants (POPs)*: Jae-Ho Yang, editor, **2001**, *50*, 272-275.

8. C. Marvin, M. Alaee, S. Painter, M. Charlton, P. Kauss, T. Kolic, D. Takeuchi and E. Reiner. Persistent organic pollutants associated with suspended sediments in the western Lake Erie – Detroit River corridor. *Proceedings of 21st International Symposium on Halogenated Environmental Organic Pollutants and Persistent Organic Pollutants (POPs)*: Jae-Ho Yang, editor, **2001**, *51*, 195-198.

9. J-P.F. P. Palmentier and Vince Y. Taguchi. The determination of six taste and odour compounds in water using Ambersorb 572 and high resolution mass spectrometry. *Analyst* **2001**, *126*, 840-845.

10. Sylvia Cussion and Sathi Selliah. Interlaboratory study 99-2: Polychlorinated Dibenzo-p-Dioxins, Polychlorinated Dibenzofurans and Dioxin-like Polychlorinated Biphenyls in Solid Matrices. Ministry of Environment, Laboratory Services Branch Report; **2001**, Queen's Printer for Ontario (ISBN 0-7794-1863-8).

11. Sylvia Cussion. Interlaboratory study 2000-1: Toxaphene Standards and Air Sample Extract. Ministry of Environment, Laboratory Services Branch Report; **2001**, Queen's Printer for Ontario (ISBN 0-7794-1861-1).

B. Presentations

1. *K.A. MacPherson*, E.J. Reiner and T.M. Kolic. Dual microbore column GC/HRMS analysis of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DLPCBs). Presented at: *21st International Symposium on Halogenated Environmental Organic Pollutants and Persistent Organic Pollutants (POPs),* September 10, 2001, Gyeongju, Korea.

2. T.M. Kolic and E.J. Reiner. An investigation of Aroclor Mixtures and their dioxin-like PCB (DLPCB) congener contributions. Presented at: *21st International Symposium on Halogenated Environmental Organic Pollutants and Persistent Organic Pollutants (POPs),* September 13, 2001, Gyeongju, Korea.

3. *C. Marvin*, M. Alaee, S. Painter, M. Charlton, P. Kauss, T. Kolic, D. Takeuchi and E. Reiner. Persistent organic pollutants associated with suspended sediments in the western Lake Erie – Detroit River corridor. Presented at: *21st International Symposium on Halogenated Environmental Organic Pollutants and Persistent Organic Pollutants (POPs),* September 13, 2001, Gyeongju, Korea.

4. J.B. Plomley, Y. Mouget, P. Crozier and *V. Taguchi*. Separation and quantitation of nonylphenol and nonylphenol polyethoxylates by triple-stage quadrupole mass spectrometry coupling normal phase chromatography – APCI with multiple-

reaction monitoring. Presented at: *49th American Society for Mass Spectrometry Annual Conference*, May 26-31, 2001, Chicago, USA.

5. *P.W. Crozier*, V.Y. Taguchi, J.B. Plomley and Y. Mouget. Analysis of nonylphenol and nonylphenol ethoxylates in complex matrices using liquid chromatography – tandem mass spectrometry. Presented at: *14th Tandem Mass Spectrometry Workshop*, Nov. 26-Dec. 1, 2001, Lake Louise, Alberta.

6. *Barry Ali*, Ernie Chen and Larry Matchuk. A comparison of LLE ve SPE, and GC-TSD vs GCMSD for the analysis of triazines in soils, vegetation, and chlorinated water. Presented at: *Western Canada Pesticide Residue Conference*, May 27, 2001, Winnipeg, Manitoba.

7. *Chris Marvin*, Mehran Alaee, Eric Reiner, Karen MacPherson, Terry Kolic and Peter Kauss. Persistent oganic pollutants in Detroit River suspended sediments: polychlorinated naphthalenes, polychlorinated dibenzo-p-dioxins and dibenzofurans, and co-planar PCBs. Presented at: *47th International Conference on Analytical Sciences and Spectroscopy*, Aug. 20, 2001, Toronto, Canada.

8. *K.A. MacPherson*, E.J. Reiner and T.M. Kolic. Dual microbore GC/HRMS analysis of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DLPCBs). Presented at: *47th International Conference on Analytical Sciences and Spectroscopy*, Aug. 22, 2001, Toronto, Canada.

9. *Tony Chen*, Mary Ann Bogard and Eric Reiner. The determination of organochlorine pesticides (OCs) and toxaphenes in environmental samples using Fast GC. Presented at: *47th International Conference on Analytical Sciences and Spectroscopy*, Aug. 22, 2001, Toronto, Canada.

10. *Chunyan Hao*, Paul Yang and Raymond E. March. Interesting behavior of salt solutions in electrospray mass spectrometry. Presented at: *47th International Conference on Analytical Sciences and Spectroscopy*, Aug. 22, 2001, Toronto, Canada.

11. *T.M. Kolic*, E.J. Reiner and K.A. MacPherson. Dioxin-like PCB (DLPCB) contributions in environmental samples: an identification technique for Aroclor mixtures. Presented at: *47th International Conference on Analytical Sciences and Spectroscopy*, Aug. 21, 2001, Toronto, Canada.

12. *Stephanie Lemanik*, M. Wilson, C. Hartley, D. Boyd and P. Yang. ppq determination of PCB congeners, organochlorines and PAHs by a benchtop GC/MS system. Presented at: *40th Eastern Analytical Symposium and Exposition*, October 1-4, 2001, Atlantic City, N.J.

13. *E.J. Reiner*, A.R. Boden, G.E. Ladwig. Analysis of Polycyclic Aromatic Compounds using Microbore Columns. Presented at: *International ISPAC Conference*, September, 2001, Cincinnati, USA.

14. *Ray Clement*. The future of trace analysis. Presented at: *2001 AOAC Annual Meeting and Exposition*, September 10, 2001, Kansas City, USA.

15. *Ray Clement*. How to apply for a co-op job. Presentation made to University of Guelph environmental science co-op students, February 26, 2001, Guelph, ON.

16. *Ray Clement*. Career success. Presentation made to University of Toronto, Institute of Environmental Studies students for *Career Day*, March 21, 2001, Toronto, ON.

17. *Ray Clement*. Job hunting: what employers expect. Presentation made to clients of *Accessible Community Counselling & Employment Services* (ACCES), March 22, 2001, Toronto, ON.

18. *Ray Clement*. Employment opportunities and networking. Presentation made to clients of *Executive Advancement Resources Network* (EARN), May 22, 2001, Toronto, ON.

19. *Ray Clement*. Career and life success. Address presented at convocation ceremony, Monsignor Percy Johnson high school, June 26, 2001, Toronto, ON.

20. *Ray Clement*. Careers in environmental science. Presentation made to University of Toronto (Scarborough campus) environmental club: *Second Nature*, November 27, 2001, Scarborough, ON.

21. *Ray Clement*. Environmental career success factors . Presentation made to University of Toronto forestry graduate students, November 29, 2001, Toronto, ON.

C. LSB Staff Recognition – 2001

1. MOE – Emerald Award Recipients:
   Quality Service: *Rhonda Schop*, Senior Microbiology Scientist; *Sylvia Cussion* and *Sathi Selliah*, Quality Management Unit
   Career Achievement: *Bern Schnyder*, Director

2. MOE – Environmental Sciences & Standards Division Awards:
   Outstanding Achievement: Infrared Spectroscopy Group, *Peter Jones, Ralph Ruffolo, Alina Sims*
   Outstanding Publication: *Vince Taguchi* [publication #2]; *Lorna Grey, Bick Nguyen, Paul Yang* [publication #4]; *Karen MacPherson, Eric Reiner, Terry Kolic* [publication #6]

3. Laboratory Services Branch Award Recipients:
   Director's Award: *David Morse*
   Customer Service Award: *Anna Pappas*
   Performance Excellence Award: Mercury Unit – Spectroscopy, *Peter Grauds, Regina Pearce, Ram Prasaud, Arthur Howlett*

F. New Analytical Methods

A. New Laboratory Services Branch Methods

1. E3423: *The Determination of Trace Metals in Road Dust by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)* [contact Peter Drouin]

2. E9002: *The Preparation of Leachates using the Toxicity Characteristic Leaching Procedure (TCLP)* [contact John Carron]

B. New Dorset Research Facility Analytical Methods

1. E3424: *The Determination of Total Kjeldahl Nitrogen in Surface Water and Precipitation by Colourimetry*